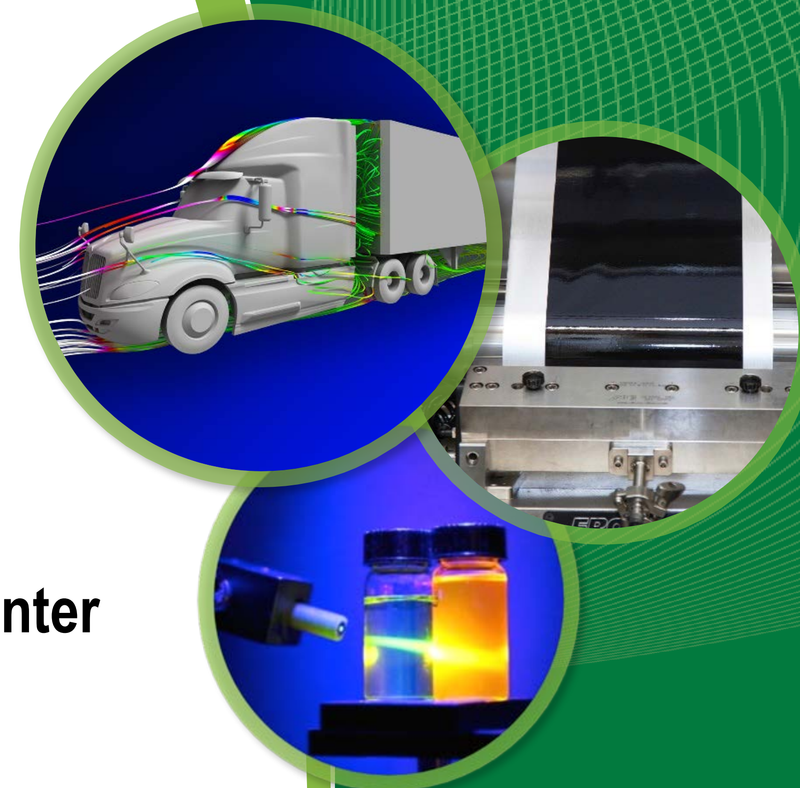
# Thick Low-Cost, High-Power Lithium-Ion Electrodes via Aqueous Processing

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**Oak Ridge National Laboratory**
**National Transportation Research Center**



**2017 U.S. DOE Vehicle Technologies Office Annual Merit Review**

**June 8, 2017** **Project ID: ES164**





ORNL is managed by UT-Battelle
for the US Department of Energy

# Overview

## Timeline

- Task Start: 10/1/14
- Task End: 9/30/19
- Percent Complete: 50%

## Barriers

- Barriers Addressed
  - **By 2022, further reduce EV battery-pack cost to $125/kWh.**
  - **Advanced Li-ion HEV/PHEV battery systems with low-cost electrode architectures.**
  - **Achieve deep discharge cycling target of 1000 cycles for EV 2022**

## Budget

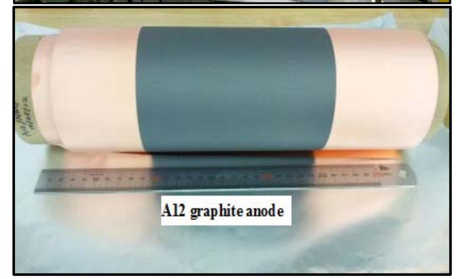
- Total task funding
  - $3600k
- $700k in FY16
- $700k in FY17

## Partners

- Interactions/Collaborations
  - National Laboratories: ANL, SNL, INL
  - Universities: KIT, SUNY-Binghamton, Purdue University, Texas A&M University
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Material/Process Suppliers: PPG Industries, TODA America, Superior Graphite, GrafTech International, IMEYS, JSR Micro, Solvay Specialty Polymers, SABIC Global Technologies, Ashland, PneumatiCoat
  - Equipment Manufacturer: Frontier Industrial Technology, B&W MEGTEC, DataPhysics
- Project Lead: ORNL

# Relevance & Objectives

- Main Objective: To improve cell energy and power density and reduce battery pack cost by manufacturing thick electrodes via aqueous processing.
  - Replace NMP processing with water-based chemistry ***at scale***.
  - Understand limiting performance factors in thick electrodes towards high energy and power density.
  - Investigate processibility of thick electrodes (coating integrity, substrate adhesion, particle/agglomerate cohesion, etc.).
  - Characterize and correlate surface energy of electrodes and electrolyte wetting.
  - Correlate electrode structure with cell performance.
  - Optimize power density by controlling particle size distribution, electrode porosity, pore size distribution, porosity gradients and tortuosity.
- Relevance to Barriers and Targets
  - Correlate ***aqueous*** colloidal dispersion properties and ***thick*** electrode coatings to cell performance to reduce LIB pack cost.
  - Increase energy density to >>200 Wh/kg (cell level)
  - ***Preserve*** long-term performance: achieve a lifetime of 10 years and 1000 cycles at 80% DOD for EVs and 5000 deep discharge cycles for PHEVs.

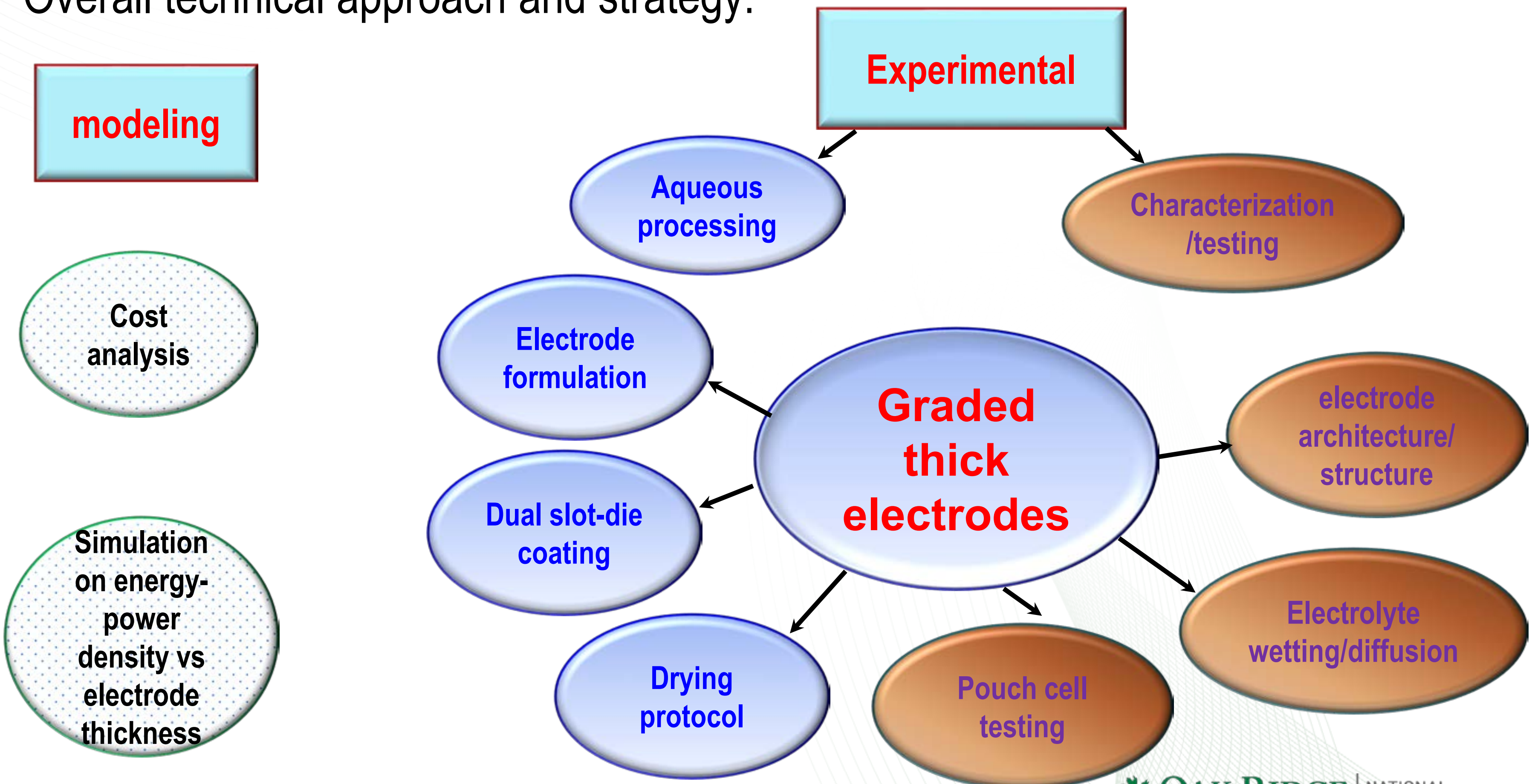



# Project Milestones

| Status | SMART Milestones | Description |
|---|---|---|
| 3/2017 | Stretch Milestone | Complete 1.5-Ah pouch cell rate performance, low-rate cycling (50 0.2C/-0.2C cycles), and high-rate cycling (150 1C/-2C cycles) for cells with aqueous ABR anode and first design of aqueous, graded cathode architecture with NMC 532 → improve gravimetric energy density of baseline cell design to ≥180 Wh/kg (cell level) and demonstrate no more than 10% capacity fade through 100 additional 0.33C/-0.33C cycles in 1.5-Ah full pouch cells. |
| 3/31/17<br>To be completed by May | Annual Milestone | Quantify electrolyte uptake rate (via Washburn absorption) to determine electrode wettability for at least 3 different anodes and 3 different cathodes as a function of electrolyte constituents and binder type.” |
| 9/2017 | Go/No-Go Decision (On Schedule for Go) | Gen 1 Cathode Performance Criteria: complete 1.5-Ah pouch cell rate performance, low-rate cycling (50 0.2C/-0.2C cycles), and high-rate cycling (150 1C/-2C cycles) for cells with ***combined Gen 1 anode and cathode design of graded electrode architecture*** → improve gravimetric energy density of baseline cell design to ≥200 Wh/kg (cell level) and demonstrate no more than 20% capacity fade through 200 additional 0.33C/-0.33C cycles in 1.5-Ah full pouch cells. If Gen 1 design does not provide at least 200 Wh/kg and 80% capacity retention, move to Gen 2 materials and electrode grading design for FY18. |

# Project Approach

- Problems:
  - Excessive agglomeration and settling in aqueous dispersions.
  - Poor wetting and adhesion of water-based dispersions to current collector foils.
  - Poor electrode flexibility, integrity, and power density of thick electrodes.
- Overall technical approach and strategy:



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# Project Approach – Pilot-Scale Electrode Processing and Pouch Cell Evaluation: DOE Battery Manufacturing R&D Facility (BMF) at ORNL


Planetary Mixer (≤2 L)


Corona Plasma Treater (Surface Energy Modification)

Slot-Die Coating Line


Heated Calender (80,000 $lb_f$)

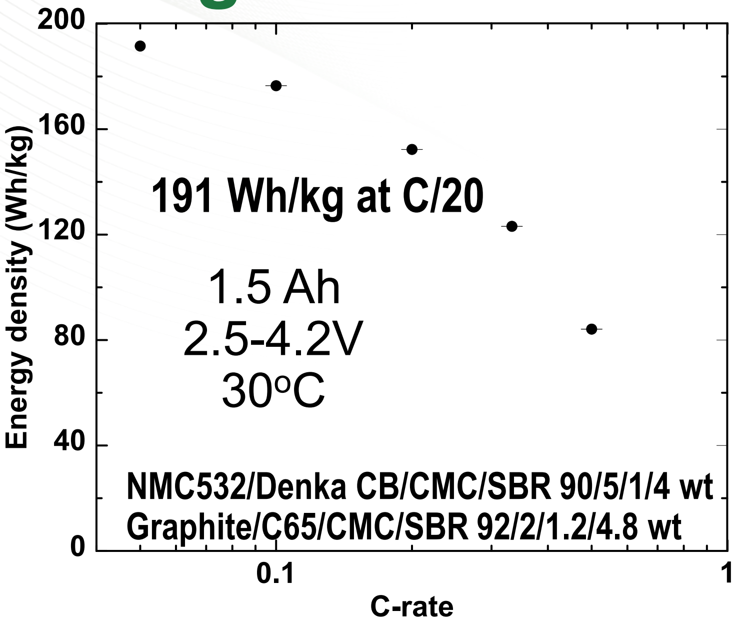
**<u>Dry room for pouch cell assembly</u>**

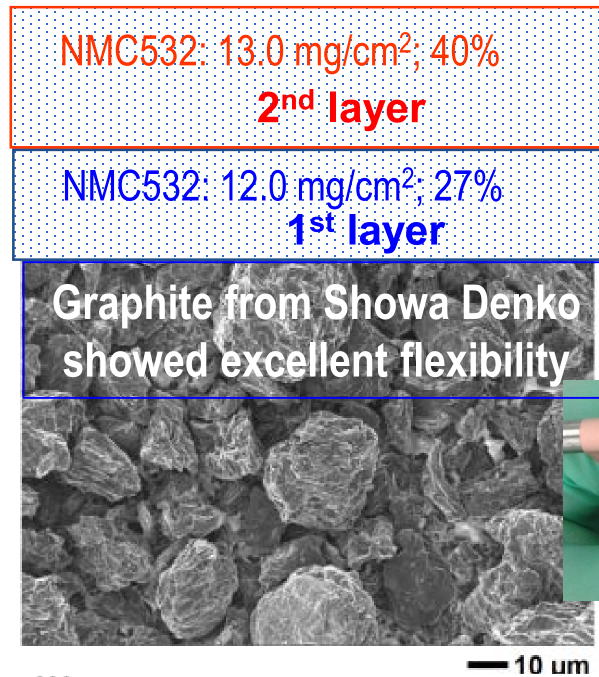
- •Largest open-access battery R&D facility in US.
- •All assembly steps from pouch forming to electrolyte filling and wetting.
- •1400 $ft^2$ (two 700 $ft^2$ compartments).
- •Humidity <0.5% (-53°C dew point maintained).
- •Pouch cell capacity: 50 mAh – 7 Ah.
- •Single- and double-sided coating capability.
- •Current weekly production rate from powder to pouch cells is 20-25 cells.

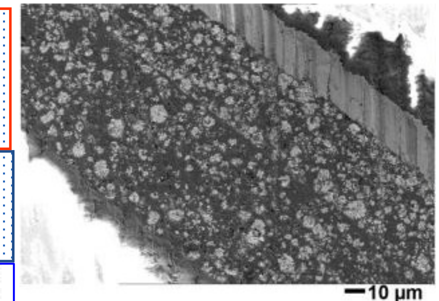
# Technical Accomplishments – Executive Summary

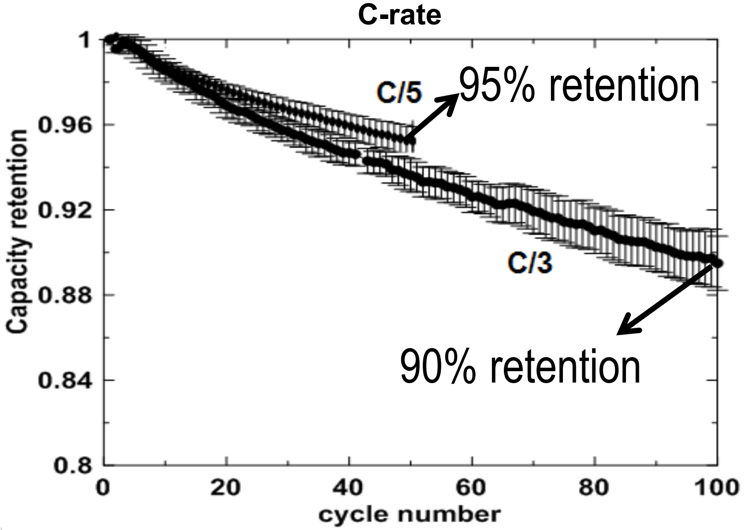
- Enabled crack-free NMC532 cathodes with 25 $mg/cm^2$ via aqueous processing.
- Demontrated191 Wh/kg in 1.5-Ah pouch cells with all aqueous processed electrodes.
- Calendar life study of 1.5-Ah pouch cells with INL.
- Built a custom experimental apparatus for electrolyte wetting study and systematically investigated electrolyte wetting with various areal mass loading.
- Created laser structured NMC532 cathode with KIT.
- Demonstrated improvement in energy and power density when replacing carbon black with carbon nanotube.
- Characterized the surface energies of individual cathode component and correlated them to the surface energy of NMC532 cathodes and electrolyte wetting.

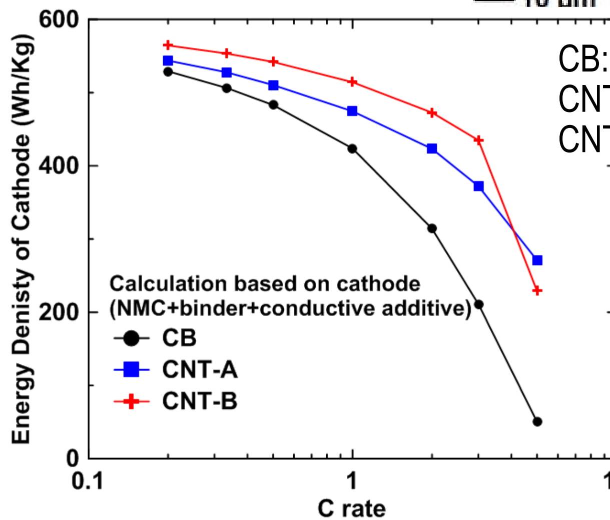
# Technical Accomplishments – Gen 1 All Aqueous 1.5-Ah Pouch Cells Demonstrated 191 Wh/kg in Cell Level




CB: CMC-SBR/CB 5/5 wt
CNT-A:CMC-SBR/CB/CNT 5/0.7/1.8 wt
CNT-B: CMC-SBR/CB/CNT 5/0.7/1.8 wt

Significant increase in energy density with partial substitution of CB with CNT



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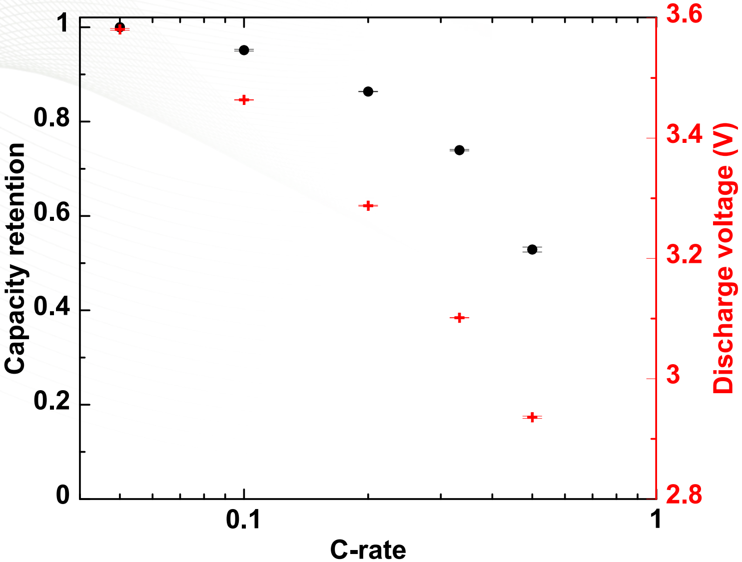
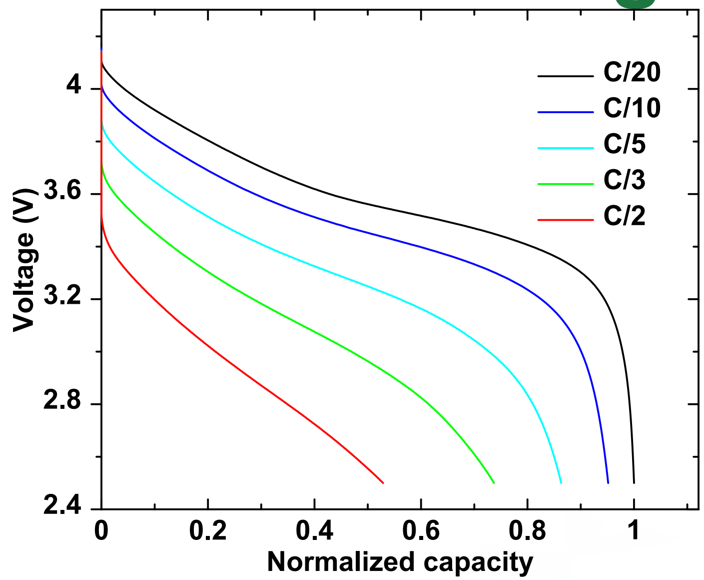
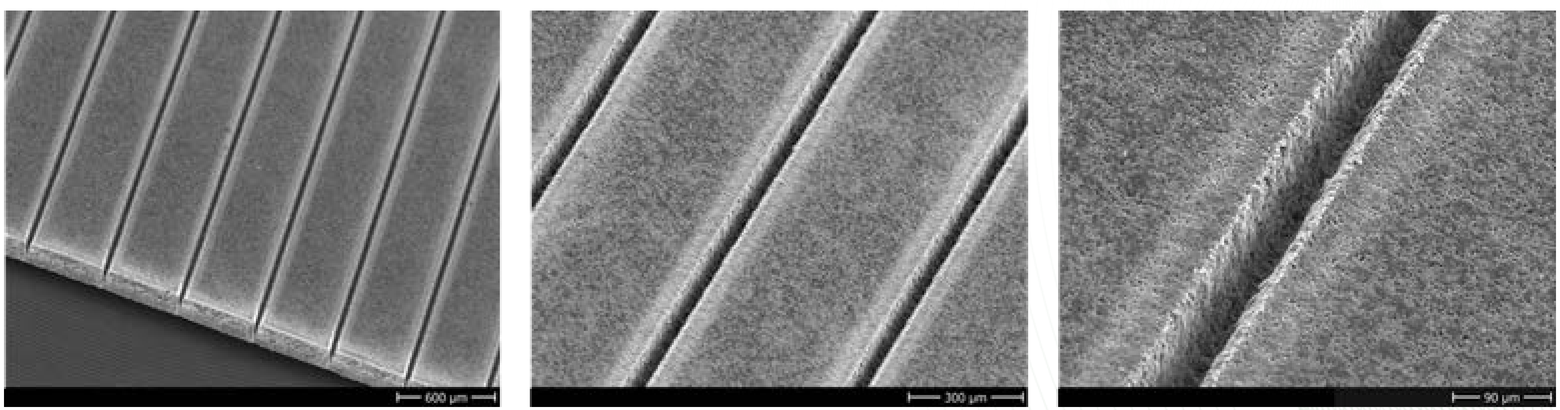
# Technical Accomplishments—Significant Polarization in Gen 1 Electrode Design



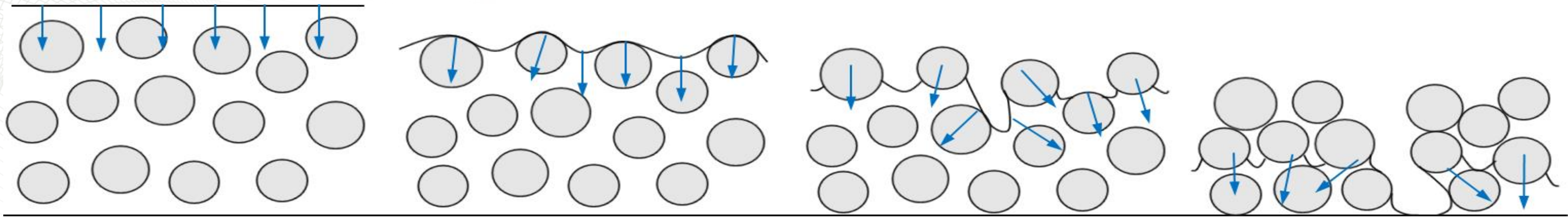




Strategies: implementation of graded electrode architecture to anode and controlling tortuosity




Laser structured NMC532 cathodes to create channels for electrolyte transport. Electrochemical performance is under testing.

# Technical Accomplishments—Insights in Electrode Cracking



**All particles are suspended in the solvent.**

**Air-solvent interface reaches the sediment surface. Menisci are formed between particles.**

**Crack initiation by in-plane pressure.**

**Crack propagation through coating**

**How thick can a coating be made without cracking?**

**R**: particle radius

**G**: shear modulus of particles

**M**: coordination number

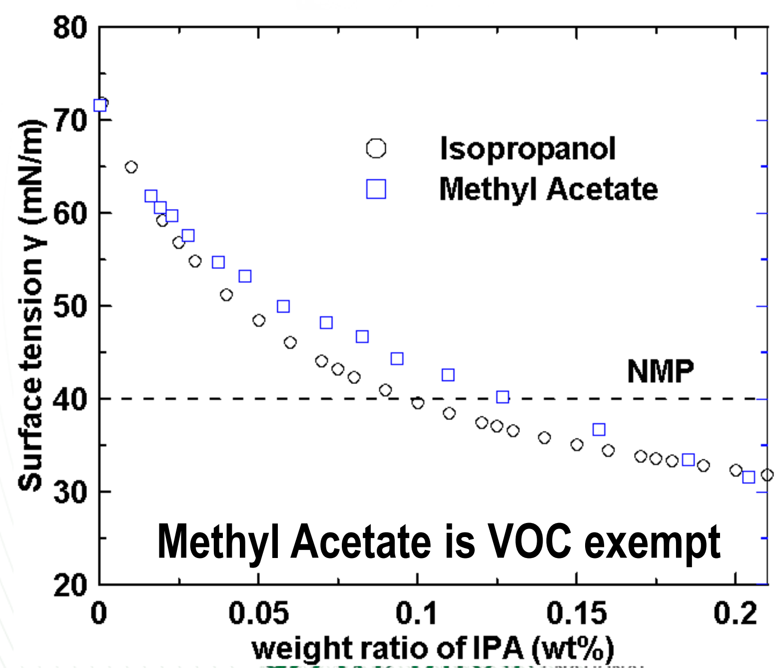
**Φ$_{rcp}$**: particle volume fraction at random close packing

$\gamma$: surface tension

$$h_{max} = 0.41\left(\frac{GM\phi_{rcp}R^3}{2\gamma}\right)^{1/2}$$

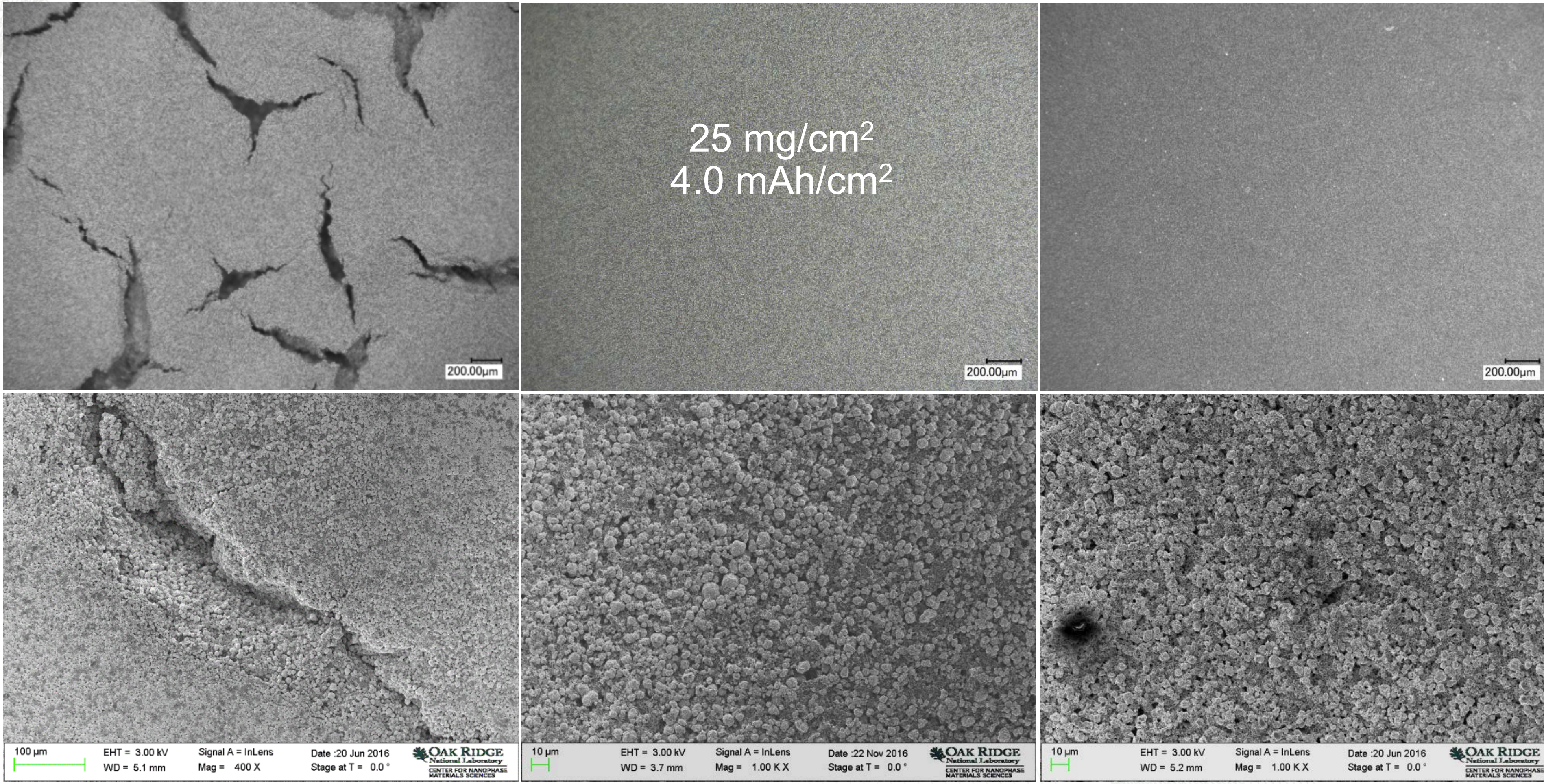
**The parameter that can be easily changed is $\gamma$–solvent surface tension.**

Du et al., *JPS*, In Press




*Anal. Chem.*, 61, 194 (1989); *J. Chem. Eng. Data* **2010,** *55,* 2905–2908

# Technical Accomplishments—Enabling Thick Electrodes (4 mAh/cm$^2$) via Aqueous Processing



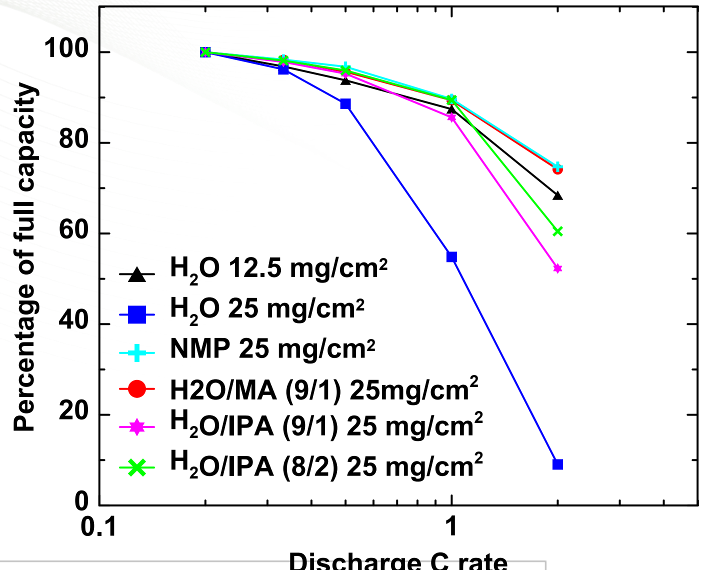

**100% water**
**Crack formation**

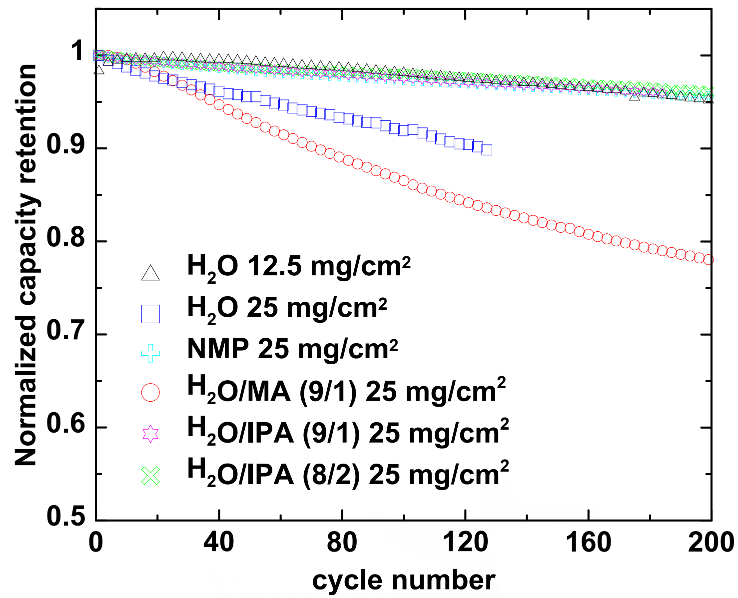
**$H_2O$/MA (90/10 wt)**
**No cracking**

**NMP/PVDF**
**No cracking**

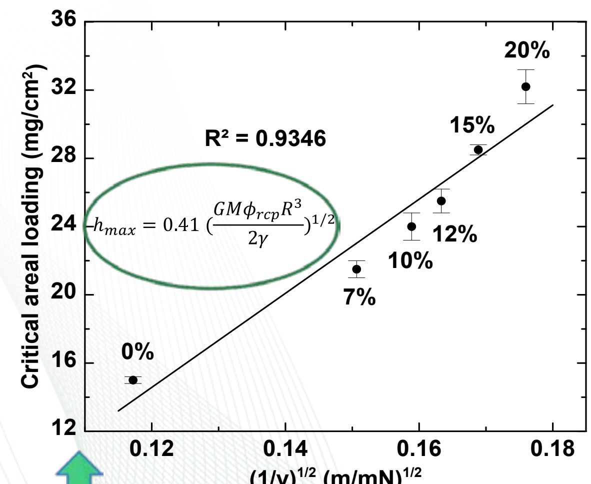
Du et al., *JPS*, In Press

# Technical Accomplishments—Excellent Rate Performance from NMC532 (4 mAh/cm$^2$) via Aqueous Processing




- Poor rate capability from cracked cathode at 25 mg/cm$^2$ with 100% $H_2O$
- Improved rate performance from cathode processed with NMP or $H_2O$/MA (9/1 wt) at 25 mg/cm$^2$
- However, the cycle life of $H_2O$/MA (9/1 wt) formulation needs to be improved.




Crack free NMC532 cathodes can be fabricated with H2O/IPA (8/2 wt) up to 32 mg/cm$^2$ (5 mAh/cm$^2$).



Du et al., *JPS*, In Press

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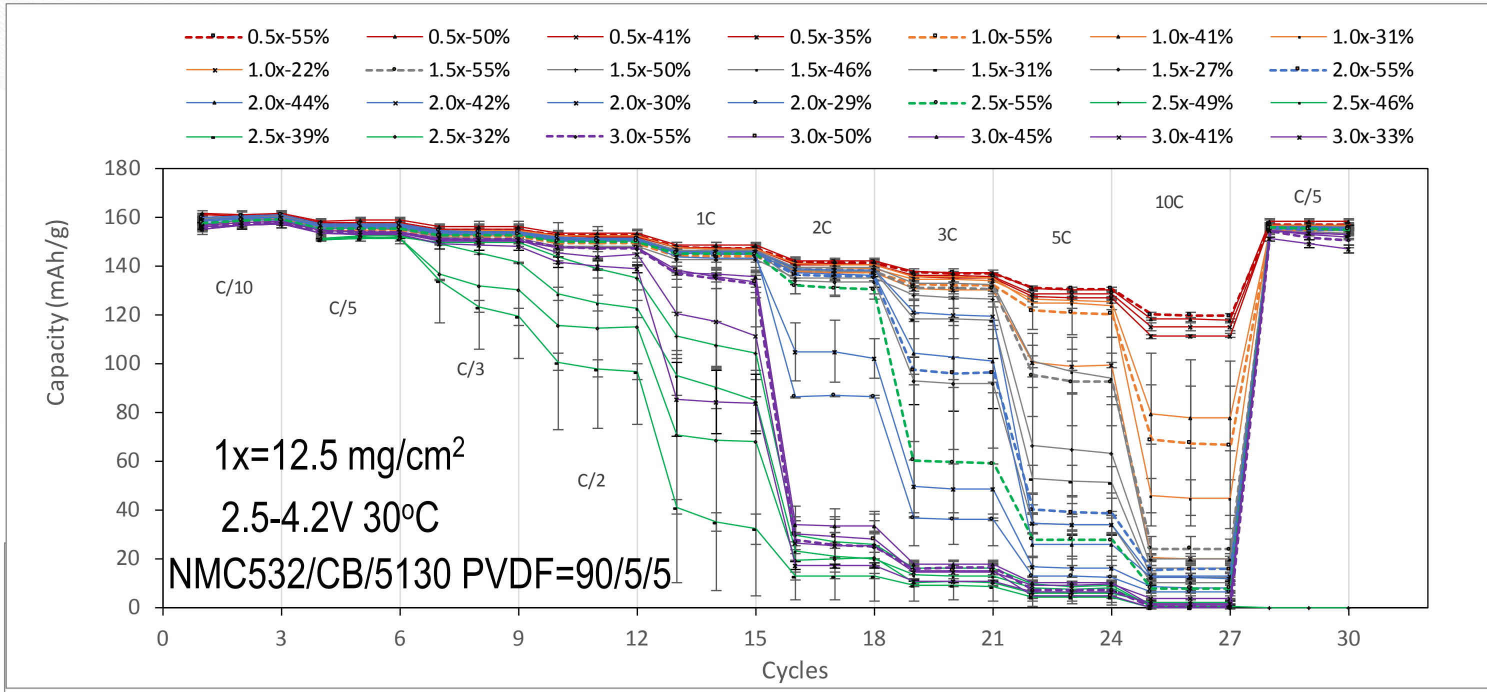
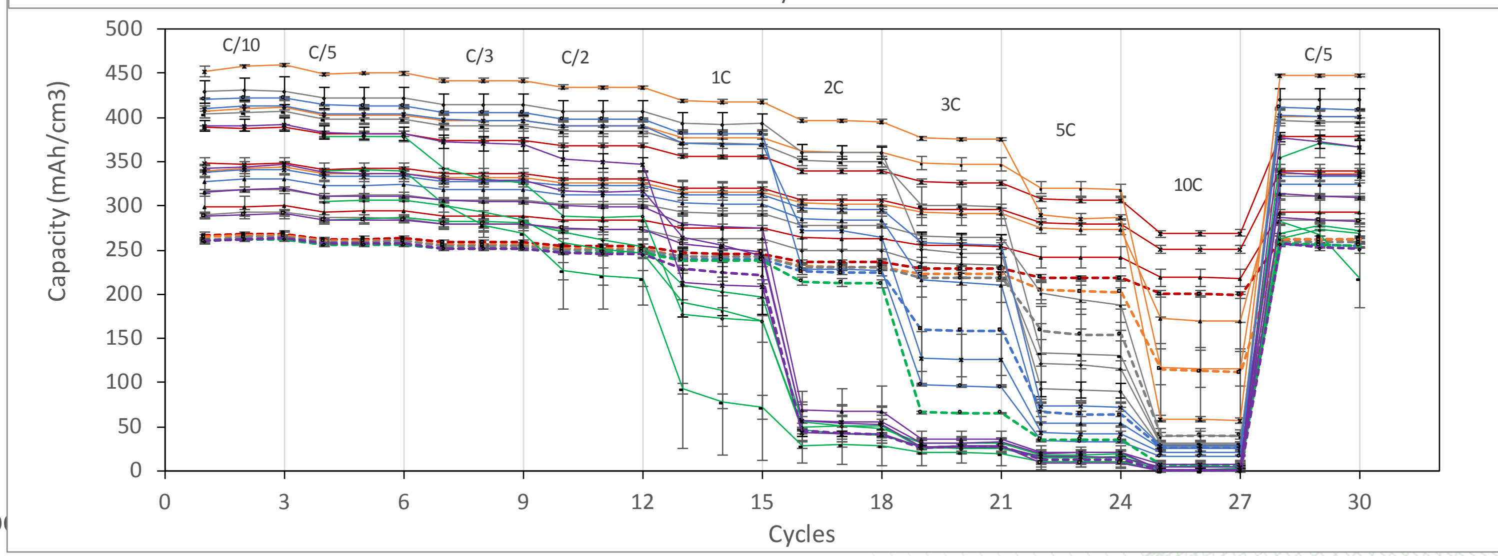
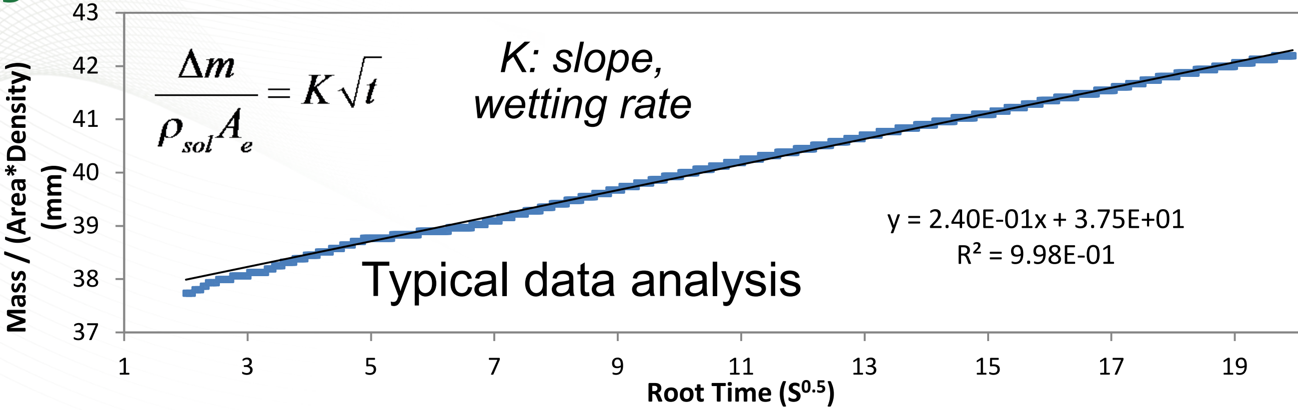
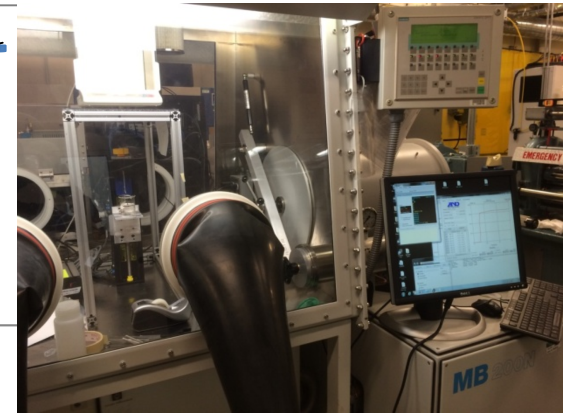
# Technical Accomplishments—Evaluation of Specific and Volumetric Capacity vs. Areal Loadings



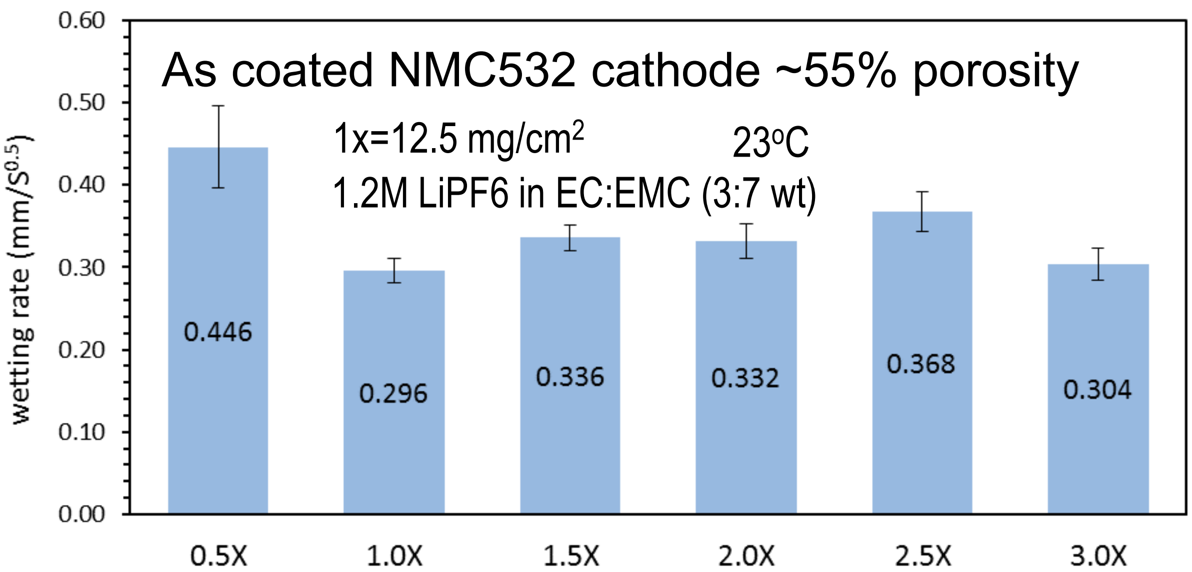



# Technical Accomplishments—Built a Setup and 1st Systematic Characterization of Electrolyte wetting



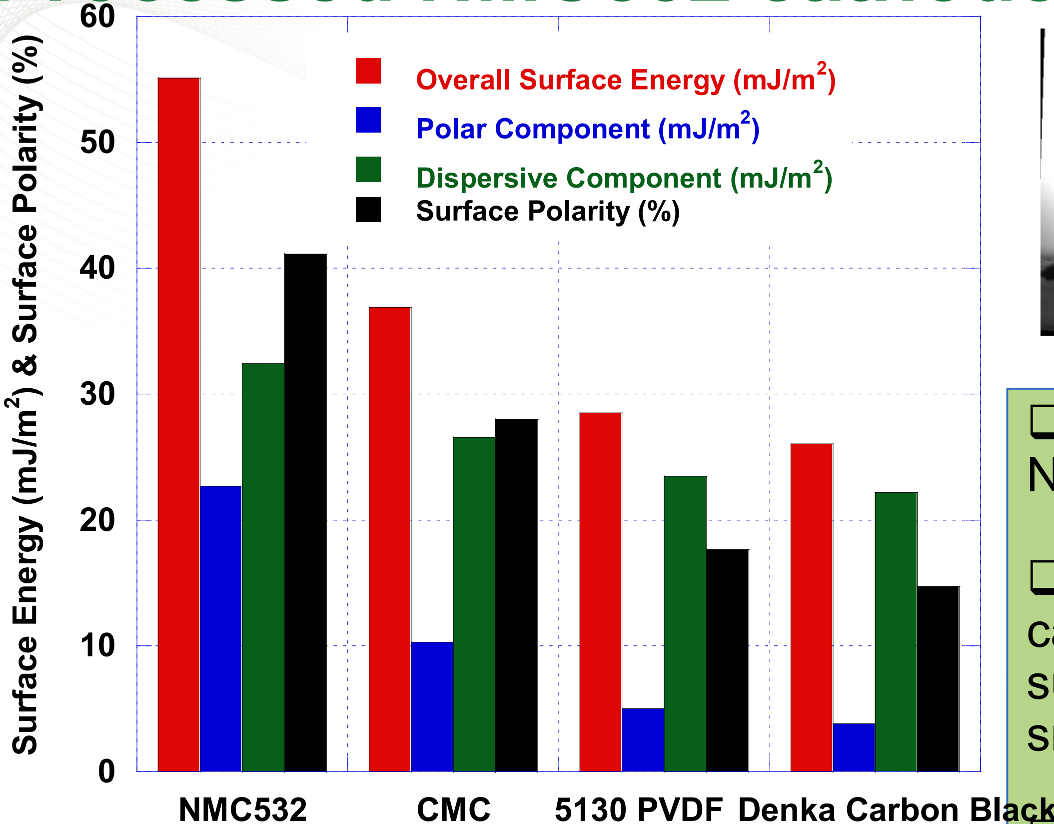



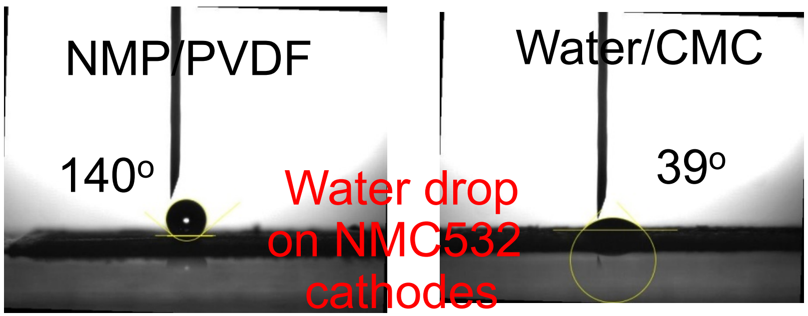

*m*: mass; *t*: time; ρ: liquid density; $A_e$: cross-sectional area of electrode




- ❑Similar electrolyte wetting rates regardless areal mass loading
- ❑Experimental error mainly due to electrolyte vaporization during test
- ❑Effect of porosity on electrolyte wetting is to be characterized
- ❑Electrolyte wetting is also characterized by dynamic wetting using a high speed camera

# Technical Accomplishments—Higher Overall Surface Energy and Surface Polarity in Aqueous Processed NMC532 cathodes




Aqueous processed NMC532 cathodes allows for shorter aging period during formation cycles.

- ❑Surface energy of each component in NMC532 cathodes were characterized.
- ❑Aqueous processed NMC532 cathodes—higher surface energy and surface polarity evidenced by the much smaller contact angle with water.
- ❑Enhanced electrolyte wetting on aqueous processed NMC532 cathodes since common electrolyte solvents have high surface polarity.



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# Collaborations

- Partners
  - National Labs: Argonne National Laboratory, Sandia National Laboratory, Idaho National Laboratory
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Active Material Suppliers: TODA America, Superior Graphite, GrafTech International , PneumatiCoat
  - Inactive Material Suppliers: JSR Micro, Solvay Specialty Polymers, SABIC Global Technologies, Ashland, IMERYS
  - Equipment/Coating Suppliers: PPG Industries, Frontier Industrial Technology, B&W MEGTEC, DataPhysics
  - Universities: KIT, SUNY-Binghamton, Purdue University, Texas A&M University

- Collaborative Activities
  - Electrolyte volume effect, cell assembly standard, and formation protocol effect on SEI with ANL
  - Calendar life evaluation with INL
  - Selection of appropriate dispersants and water-soluble binders for aqueous processing and thick electrode development (with Solvay Specialty Polymers, JSR Micro, and Ashland).
  - Drying economics and capital expense quantification for water vs. NMP-based electrode drying (B&W MEGTEC and ANL).
  - Characterization of surface energy and electrolyte wetting with SUNY-Binghamton and Data Physics
  - Fabrication of thick electrode and electrode architecture with Texas A&M and KIT

# Future Work

- Remainder of FY17
  - Characterize electrolyte wetting vs porosity in electrodes via aqueous and NMP-based processing.
  - Integrate Gen 1 anode and cathode design with graded structure.
  - Deconvolute the contribution of individual component on the electrode surface energy.
  - Fabricate thick electrodes with various active material particle size.
  - Continue to evaluate calendar life of pouch cells with aqueous processed electrodes.
  - Integrate laser structured anode and cathode for high power densities.
- Into FY18
  - Estimate maximum energy and power density of NMC532 and graphite.
  - Correlate electrode processing and electrolyte wetting.
  - Continue formulation development and scale-up work with PPG Industries.
  - Continue obtaining 2000 USABC capacity fade cycles at 0.33C/-0.33C for for different thick coating strategies.
- Commercialization: Highly engaged with potential licensees; high likelihood of technology transfer because of significant cost reduction benefits and equipment compatibility.

*Any proposed future work is subject to change based on funding levels*

# Summary

- **Objective:** This project facilitates lowering the unit energy cost by up to 17% for EVs and PHEVs by addressing the expensive electrode coating and drying steps while simultaneously increasing electrode thickness.
- **Approach:** Blends colloidal and surface science with manufacturing science (coating, drying, etc.) and electrode engineering to enable implementation of aqueous processed thick electrodes for high power performance.
  - Processing and capital cost savings for aqueous processed thick electrodes are addressed.
  - Electrode formulation and processing are developed to enable thick electrode manufacturing.
  - Drying protocols are developed for electrode integrity and homogeneity.
  - Electrode architecture is optimized for appropriate power density.
- **Technical:** Scale up manufacturing of water-based NMC532 and graphite electrodes; Demonstrated cycle life in 1.5-Ah pouch cell with both NMP and water-based NMC532 and CP A12; Enabled thick electrodes via multiple coatings or dual slot-die coating; Characterized porosity gradient effect on power density and surface energy effect on electrolyte wetting.
- **Collaborators:** Extensive collaborations with national laboratories, universities, lithium-ion battery manufacturers, raw materials suppliers, and coating producer.
- **Commercialization:** Highly engaged with potential licensees; high likelihood of technology transfer because of significant cost reduction benefits and equipment compatibility.

# Selected Responses to Specific FY16 DOE AMR Reviewer Comments

- Second reviewer recommended incorporating statistical analysis tools, comparing results for different cathode materials and benchmarking.
  - The benchmarking for this project is NMC532 and graphite chemistry with 1.8-2.0 mAh/cm$^2$ which has been established through round robin test among ORNL-ANL-SNL.
  - The selected cathode materials is NMC532 by the ABR program. We are evaluating aqueous processing with other NMC compositions such as NMC622 and NMC811.
- Second reviewer identified that the initial evaluation may not include all the improvement enabled from the aqueous processing.
  - The reviewer was right. Some of the benefits enabled from the aqueous processing were not fully included, such as green manufacturing and less environmental effect.
- First review identify that it's necessary to address and justify the significantly lower cost reduction expectations to move further.
  - The cost reduction from aqueous processing and thick electrodes have been evaluated and the results have been published in *Journal of Power Sources* 275 (2015) 234-242. Based on our study, the cost reduction would be up to 17% in pack level.
  - We further investigated the benefits in reducing energy consumption during electrode processing . It has been demonstrated that 15% less energy was enabled with aqueous processing during primary drying mainly due to the elimination of solvent recycling. In a best scenarios, up to 50% energy reduction could be realized. The results have been published in *Drying Technology*, In Press.

# Acknowledgements


- U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (Program Managers: David Howell and Peter Faguy)

- ORNL Contributors:
  - David Wood
  - Claus Daniel
  - Zhijia Du
  - Yangping Sheng
  - Seong Jin An
  - Marissa Wood
  - Kevin Hays
  - Jesse Andrews
  - Tommiejean Christensen

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- Robert Wang
- Congrui Jin
- Ranjan Dash
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- Mike Wixom
- James Banas
- Gregg Lytle
- Stuart Hellring
- Chong Chen
- Kejie Zhao
- Partha Mukherjee

# Information Dissemination and Commercialization

- **8 Refereed Journal Papers**

1. Luize Scalco de Vasconcelos, Rong Xu, Jianlin Li, and Kejie Zhao, “Grid indentation analysis of mechanical properties of composite electrodes in Li-ion batteries”, *Extreme Mechanics Letters*, 9 (2016) 495-502.
2. Jianlin Li, Claus Daniel, Seong Jin An, and David Wood, “Evaluation of residual moisture in lithium-ion battery electrodes and its effect on electrode performance”, *MRS Advances*, 1(15) (2016) 1029-1035.
3. Zhijia Du, David Wood, Claus Daniel, Sergiy Kalnaus, and Jianlin Li, “Understanding limiting factors in thick electrodes towards high energy density Li-ion batteries”, *Journal of Applied Electrochemistry*, 47 (2017) 405-415.
4. Hui Zhou, Ke AN, Srikanth Allu, Jianlin Li, Sreekanth Pannala, Hassian Bilheux, and Jagjit Nanda, “Probing multiscale transport and inhomogenerity in a lithium-ion pouch cell using in-situ neutron methods”, *ACS Energy Letters*, 1 (2016) 981-986.
5. Zhijia Du, Kelsey Rollag, Jianlin Li, Seong Jin An, Marissa Wood, Yangping Sheng, Partha Mukherjee, Claus Daniel, and David Wood, “Enabling aqueous processing for crack-free electrodes”, *Journal of Power Sources*, In Press.
6. Rong Xu, Luize Scalco de Vasconcelos, Jenzhe Shi, Jianlin Li, and Kejie Zhao, “Disintegration of primary particles in $LiNi_xMn_yCo_zO_2$ cathode materials”, *Experimental Mechanics*, In Press. (Invited Paper)
7. David Wood, Jeffrey Quass, Jianlin Li, Shabbir Ahmed, David Ventola, and Claus Daniel, “Technical and economic analysis of solvent-based lithium-ion electrode drying with water and NMP”, *Drying Technologies,* In Press.
8. Jianlin Li, Zhijia Du, et. al., “Towards low-cost, high energy density and high power density lithium-ion batteries” *JOM*, under review. (Invited Paper)

- **Selected Presentations**

1. **Jianlin Li**, Zhijia Du, Yangping Sheng, Claus Daniel, and David Wood, “Electrode coating via various slot-die coating techniques and associated performance”, the 18th International Coating Science and Technology Symposium, Pittsburgh, PA, September 18th- 21st.

# Technical Back-up Slides

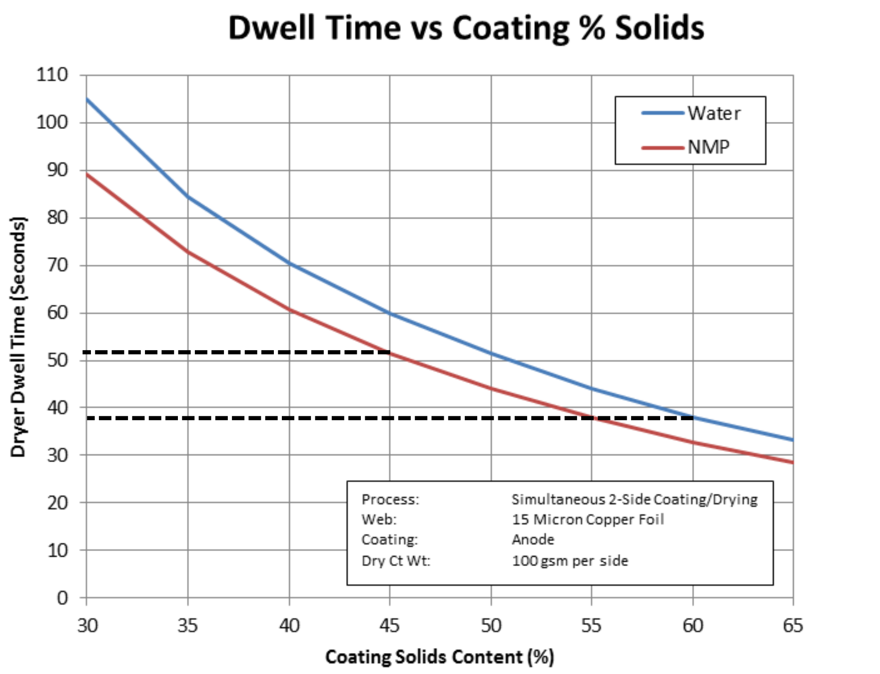
# Dual Slot-Die Coating to Reduce Interfacial Resistance

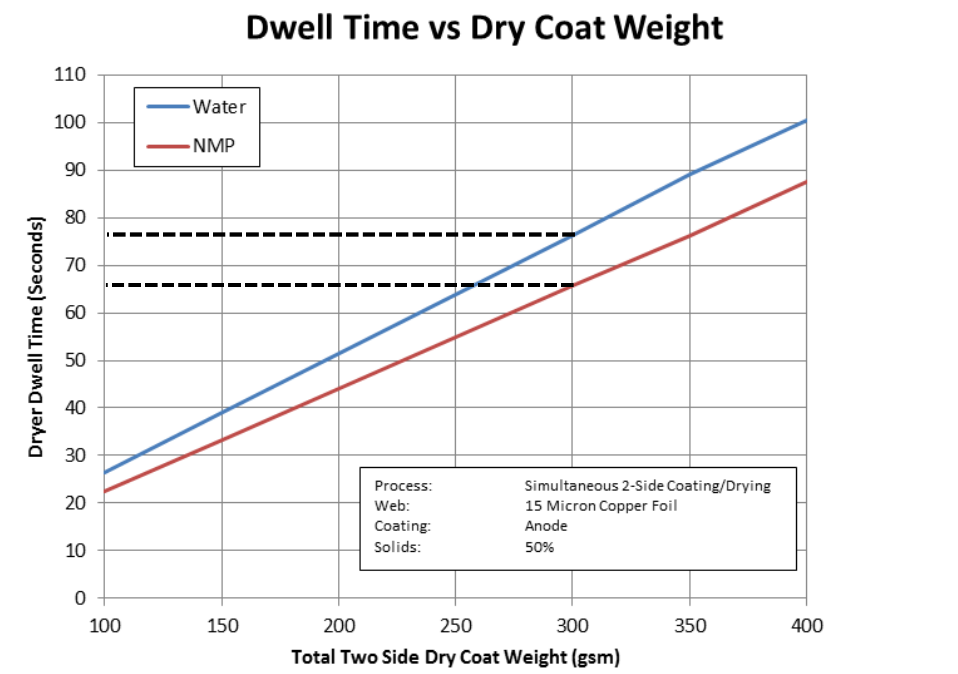
- Allows you to coat two layers on top of one another simultaneously
  - Can have two different slurry compositions


Coating lips

# Technical Accomplishments – Energy Consumption in Primary Drying

B&W MEGTEC

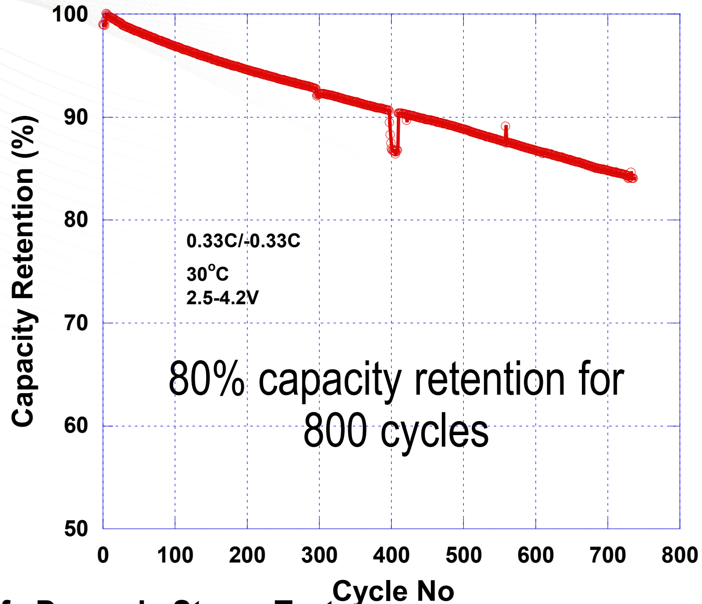


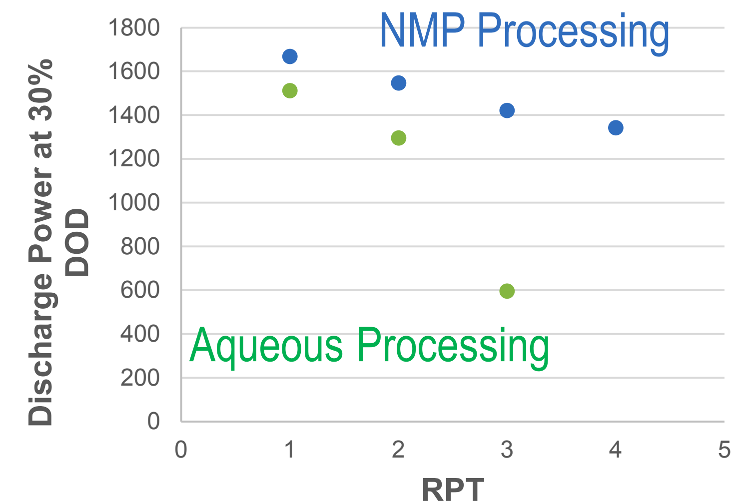



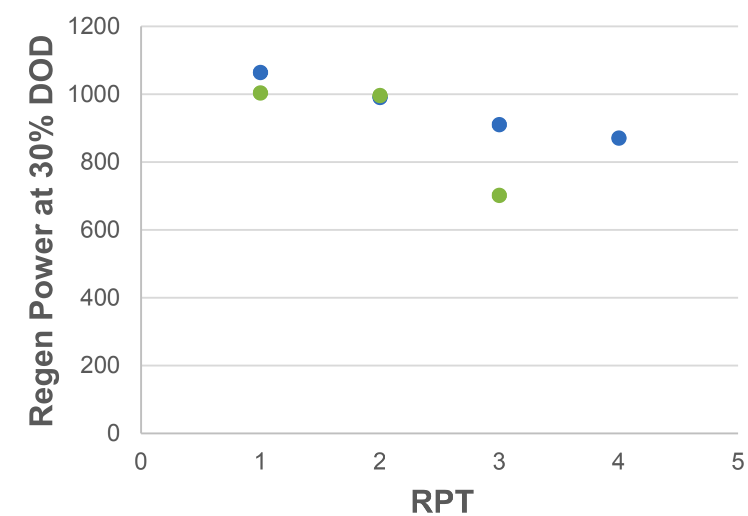

| Processing Step | NMP (kcal/m$^2$-web) | Water (kcal/m$^2$-web) |
|---|---|---|
| Wet Coating Heat Load | 84.3 | 272 |
| Dryer Heat Load | 1067 | 1351 |
| Solvent Recovery | 751 | NA |
| **Total Heat Load** | **1902** | **1623** |

- A 14.7% reduction for base case, which is far less than the 26× reduction proposed by Wood et al., *JPS*, **275**, 234 (2015).
- Best case scenario for aqueous processing (with optimized conditions) is likely a 2× energy consumption reduction.

# Technical Accomplishments – All Aqueous 1.5-Ah Pouch Cells Demonstrates Excellent Cycle Life, But Calendar Life Needs Further Evaluation




**Cycle Life Dynamic Stress Test**

Perform this test on the three cells:

1. Scale the test profile by 700W/kg power/weight level. If the scaling results in currents exceeding maximum current levels, use a power equal to 2 times the energy of the cell from $V_{maxop}$ to $v_{min0}$
2. Charge the devices to fully $V_{maxop}$ at 30°C
3. Rest for 15 minutes
4. Apply the DST profile until 45kWh BSF scaled energy is removed
5. Rest for 15 mintues and then charge the device back to $V_{maxop}$. Steps 3 to 5 is the equivalent of one DST Cycle
6. 100 DST cycles between RPTs

RPT—reference performance test; every 32 days

More tests are undergoing